

## Chapter 7

# Conclusions

### 7.1 Summary

The general subject of this work was the physisorption of hydrogen in modified carbon adsorbents. Physisorption involves the binding of an  $\text{H}_2$  molecule to a surface without the formation of a chemical bond, making it a simple and easily reversible storage method (i.e., no complicated reaction pathways). This topic has particular relevance for the ongoing effort to develop systems which store hydrogen at high densities while operating at modest temperatures. It is estimated that an adsorption enthalpy of about  $-18 \text{ kJ mol}^{-1}$  is needed to optimize the usable capacity of a physisorption storage system at room temperature [7].

Graphite intercalation compounds of the heavy alkali metals are one of the few systems that come close to meeting this optimum adsorption enthalpy. Cesium intercalated graphite was measured in Sec. 4.3 to have an average adsorption enthalpy of  $-14.9 \text{ kJ mol}^{-1}$ . The origin of this surprisingly large enthalpy is still not well understood, though it may originate from the highly polarizing environment created by electron transfer from the alkali metals to the empty graphite conduction bands. This unresolved question reflects a significant issue in the study of adsorption systems: the electrostatic and dispersion forces which dominate physisorption are notoriously difficult to treat in a first principles approach.

Strategies for increasing the hydrogen binding interaction in a modified carbon adsorbent include incorporating the following structural elements into the host structure: (1) optimally spaced graphene basal planes, held open in a pillared fashion by guest intercalate species; (2) curved graphene surfaces, such as those found in single-walled carbon nanotubes; (3) chemically modified carbon adsorbents, which interact with  $\text{H}_2$  molecules by strong electrostatic forces. Graphite intercalation compounds, it turns out, contain both a pillared structure *and* chemical dopants. Separating the effects of these two distinct structural elements poses a separate challenge.

Pressure-composition-temperature diagrams of the  $\text{MC}_{24}(\text{H}_2)_x$  system were measured for  $M = \text{K}, \text{Rb}, \text{Cs}$ . Temperatures were between 77 K and 150 K. Detailed adsorption enthalpies were measured as a function of  $\text{H}_2$  concentration. The enthalpy for all three systems is remarkably flat as a function of hydrogen composition. This is attributed to a fairly homogeneous distribution of sorption sites in the graphite intercalates. The adsorption enthalpy is positively correlated with the interlayer spacing of the GIC. At large  $\text{H}_2$  concentrations the adsorption kinetics becomes exceedingly sluggish, due in part to the effects of site-blocking and correlation on the microscopic  $\text{H}_2$  self-diffusivity.

Hydrogen diffusivity in  $\text{KC}_{24}$  was studied in detail by quasielastic neutron scattering and empirical molecular dynamics calculations. The QENS spectra were fitted to a model for jump diffusion on a two-dimensional honeycomb net. It was found that the diffusion coefficients for  $\text{H}_2$  are over an order of magnitude slower than those for  $\text{H}_2$  diffusion in other carbon sorbents such as single-walled nanotubes, nanohorns, and carbon blacks. Instead, the diffusivity in  $\text{KC}_{24}$  is about the same magnitude as in zeolites with molecular-sized cavities. This means that  $\text{H}_2$  diffusion in adsorbents is influenced very strongly by the pore geometry, and less by the chemical nature of the pore surface. Furthermore, the diffusion

process is very complex, with the presence of at least two distinct jump frequencies.

High-resolution inelastic neutron scattering spectra for  $\text{KC}_{24}(\text{H}_2)_x$  were collected for the first time over the *entire* energy-loss range spanning 0 meV to 100 meV. Spectral peaks were interpreted in terms of single- and multi-excitation transitions of the  $\text{H}_2$  phonon and rotational modes. Rotational energy levels were calculated from the one-dimensional hindered rotor model, while phonon energy levels were estimated from first-principles calculations. Evidence was found for the existence of multiple  $\text{H}_2$  sorption sites in  $\text{KC}_{24}$ . Further refinements of the calculations of  $\text{H}_2$  phonon and rotational energy levels are needed. Contributions from the large zero-point motions of the bound  $\text{H}_2$  molecules also need to be integrated into the model.

## 7.2 Future work

### 7.2.1 Thermodynamic trends

For the  $\text{MC}_{24}$  compounds, the hydrogen adsorption enthalpy is positively correlated with the size of the intercalant ( $\text{Cs} > \text{Rb} > \text{K}$ ). The fundamental principles behind this trend are still unclear. Dispersion forces are expected to become larger with atomic mass due to the greater number of electrons. Trends in electrostatic interactions are less clear, since we would expect the larger alkali metal atoms to have greater screening of the nuclear charge. The relative contribution of dispersion and electrostatic forces on the total binding energy therefore needs to be clarified. Variations in the charge transfer between different alkali metals and the graphite, determined quantitatively from the ground state electron density (from DFT calculations), can provide useful information on this topic. Trends in the dispersion interactions can be studied by introducing a semi-empirical van der Waals

correction to the GGA functional, as implemented in the CPMD code [119].

### 7.2.2 Two-dimensional diffusion

Past neutron scattering studies of H<sub>2</sub>-GIC systems almost exclusively use polycrystalline GIC samples. This substantially complicates the quasielastic analysis since it introduces a powder average into the jump diffusion model. Further, it reduces the amount of information that can be directly extracted from the QENS data. Single crystal GIC samples can be synthesized from monolithic HOPG pieces and then stacked together to form a bulk sample. This strategy should allow us to obtain direct information on the characteristic geometries and frequencies of the adsorbed H<sub>2</sub> dynamics without the need for orientational averages. Diffusion is expected to be two-dimensional, and this should be directly measurable with single-crystal samples. In order to successfully explain the quasielastic peak shape, we must develop a jump diffusion model incorporating a distribution of jump frequencies.

### 7.2.3 Translational-rotational coupling

A valid model must explain *all* the peaks in the IINS spectrum of KC<sub>24</sub>(H<sub>2</sub>)<sub>x</sub>, including peaks at intermediate energies. An attempt was made in this thesis to interpret the peaks in terms of single- and multi-excitations of phonon and rotational modes. However, large inadequacies remain with this model. A relevant model must take into account the strong coupling between rotations and translations of the H<sub>2</sub> molecule. A promising approach is to use first-principles based path integral molecular dynamics (PIMD) to obtain both the center-of-mass and rotational trajectories as a function of real time while also incorporating the effect of quantum delocalization. This work is computationally costly, but highly-scalable *ab initio* MD codes have recently become available which make them feasible [120].